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ABSTRACT

Information is presented about the problems involved in using sea water in the steam propulsion systems of large, modern ships. Discussions supply background chemical information concerning the problems of corrosion, scale buildup, and sludge production. Suggestions are given for ways to maintain a good water treatment program to effectively deal with these problems. (CS)

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SOME THOUGHTS ABOUT WATER ANALYSIS IN SHIPBOARD STEAM PROPULSION SYSTEMS FOR MARINE ENGINEERING STUDENTS

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INTRODUCTION

Nearly all the water used on large, modern ships comes from the sea, yet because of its dissolved minerals sea water is unsuitable for use in steam propulsion systems. Before it can be used, the dissolved materials must be removed. To accomplish this end evaporators have been incorporated in shipboard engineering systems and all water passes through them prior to its use. However, the distillation process is imperfect; therefore some minerals are carried over into other parts of the system, where if not controlled, they cause scale formation and corrosion. In addition, dissolved oxygen and high hydrogen ion concentrations in plant water also cause corrosion. While these occurrences may not sound serious to the neophyte, corrosion and scale formation do lead to inordinately high fuel costs, plant degradation and the increased probability of plant explosions.

Corrosion and scale formation are minimized by periodic chemical and physical treatment of propulsion plant water. When water treatment should occur and how the water is actually treated are based upon data from a ship's boiler and feed water testing program. Good testing programs have at least four objectives. They strive to ascertain pH, dissolved oxygen, mineral and sludge content levels. In so doing they keep the engineer constantly abreast of: (1) the water conditions as the water proceeds through the propulsion system; (2) the type of treatment required to restore the water to a noncorrosive and nonscale forming condition; and (3) the time when propulsion plant water must be treated. However, understanding the true importance of water analysis programs surfaces only with sense of the interaction between plant health and water treatment.

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DISCUSSION

Corrosion is the conversion of metals to unwanted compounds. Iron is converted to iron oxides and hydroxides, copper to copper oxide and so on. Converting metals to such compounds results in the thinning of propulsion system parts and reduction in their thickness leads eventually to secondary problems. Water leaks develop causing increased water treatment and fuel costs (water must be added to cover leakage--additional water must be distilled). Leaky areas also provide portals through which oxygen may enter. In addition, since steam propulsion systems operate under pressure, thin parts enhance the possibility that violent ruptures will occur.

Scale is the buildup of silicates, sulfates, hydroxydes and carbonates resulting from the precipitation of unwanted constituents in the feed and propulsion water. It forms on the insides of system parts, causing ineffective heat transfer between burners and the water being heated and increasing the possibility of explosion. Poor heat transfer allows much of the heat provided per unit volume of fuel to be lost with stack gases. Thus the cost of heating water per unit volume per degree Celsius increases. Scale deposition also results in constriction of water and steam passageways and the creation of abnormally high pressures. The high pressures may cause parts, previously weakened by corrosion, to burst. With these concerns in mind, let's look more closely at a ship's steam propulsion system.

Boilers are the heart of steam propulsion systems. They are closed containers where water is boiled and converted to steam (see Figure 1).

INSERT FIGURE 1 ABOUT HERE

Efficient heat transfer between a boiler's burners and feed water (water

fed to the boiler) is produced by forcing the water through hundreds of boiler tubes. The tubes are heated by burning fuel oil (see Figure 2). The steam circulates out of the tubes, allowing cooler water to enter where it, in turn, is heated.

INSERT FIGURE 2 ABOUT HERE

In the steam production process two conditions occur to prevent maximum heat transfer through the tube walls. Improper combustion control causes carbon products to build up on the fire side of the boiler tube walls. The carbon coating insulates the tubes, preventing adequate heat transfer through their walls. On the water side of the tubes, scale formed when calcium and magnesium combine with other elements in system water, may build up slowing down heat transfer. Scale deposits may contain one or all of the following; calcium carbonate, calcium silicate, magnesium hydroxide, magnesium silicate, and calcium sulfate.

INSERT FIGURE 3 ABOUT HERE

Scale forms for several reasons. Calcium carbonate, magnesium carbonate, calcium sulfate and silicates exist naturally in some waters. In the presence of heat they enter several chemical reactions.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

$$MG(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2CO_2$$

$$MgCO_3 \longrightarrow Mg(OH)_2 + CO_2$$

$$CaSO_4 + 2H_2O \xrightarrow{\text{Heat and excess } SO_4} CaSO_4 \cdot 2H_2O$$

The products of these reactions [$CaCO_3$; $Mg(OH)_2$; and $CaSO_4 \cdot 2H_2O$] are exothermic compounds. As water temperature increases, the solubility of

exothermic compounds decreases and the compounds subsequently precipitate to form scale. Scale also forms because the forming agents are left behind when steam leaves the boiler effectively increasing their concentrations in the boiler water to the point of saturation. Once saturation is reached precipitation begins and again scale is deposited.

Several steps may be taken to avoid scale formation. The ingredients may be removed before feed water becomes boiler water. In this process, carry over of contaminants is prevented by adding chemicals to the sea water in a ship's evaporators. Impurities are prevented from forming scale because they react with the additives to form suspended non-adhering sludge (see Figure 4).

INSERT FIGURE 4 ABOUT HERE

Phosphate is a chemical often added to cause sludge formation. When a phosphate is added, it remains in solution until consumed in sludge formation. In one such addition Na_2HPO_4 and NaOH are added. Calcium ions (Ca^{++}) found in water react with Na_2HPO_4

$$5Ca^{++} + 10Cl^{-} + 3Na_2HPO_4 + NaOH \longrightarrow Ca_5(OH)(PO_4)_3 + 10NaCl + 3H_2O + Na_2HPO_4$$

and NaOH to form the suspended solid $Ca_5(OH)(PO_4)_3$ and the possibility that calcium ions will react with other agents to become ($CaCO_3$) scale is eliminated. Although phosphate remains dissolved until consumed, excess amounts can also cause problems, therefore, phosphate levels must be monitored.

Some steam leaving a boiler is lost through leaks so additional water must be added. The new water requires treatment, and so additional sludge is produced. Suspended sludge level rises gradually to the point where it

must be removed, otherwise, secondary boiler problems will occur. To prevent this situation, dissolved solid levels must periodically be monitored. Monitoring is accomplished using a total dissolved solids meter and when necessary the solids are removed through the process known as "blow down" (see Figure 5).

INSERT FIGURE 5 ABOUT HERE

Heat transfer through boiler tube walls also is affected by physical or chemical weakening of the tube wall structure caused by corrosion (see Figure 6). This occurs in the absence of other harmful agents because all metals deteriorate slowly in the presence of water as a result of autoionization.

INSERT FIGURE 6 ABOUT HERE

In the process water molecules constantly and automatically undergo ionization to produce very small H^+ ion concentrations (H^+ concentration determines the acid content) ($H_2O + H_2O \rightleftharpoons 2H^+ + 2OH^-$). Acids react with metals to cause corrosion but corrosion resulting from acid attack on metals is retarded, if not prevented, by adding chemicals to the water. Caustic soda or sodium hydroxide is such a chemical. The amount to be added depends upon the pH or hydrogen ion concentration of the water. The corrosive effects of water decrease as pH increases (increasing pH means decreasing H^+ ion concentration). Yet, caustic corrosion occurs when pH values are too high. Ideally, pH should not fall below 9 or rise beyond 12.5. From a corrosion standpoint, a pH of 11-12 is optimum; however, high OH^- concentration and dissolved solids affect steam quality. Therefore, a more practical pH range guide for various operating boiler pressures is:

Low pressures (below 250 psi) pH 11.0-11.5

Intermediate Pressures (250-900 psi) pH 10.5-11.0

High Pressures (above 900 psi) pH 9.0-10.2

Oxygen reacts with metals to form metal oxides. As previously mentioned, conversion of metals to metal oxides causes structural weakening of the metals. Iron ($3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$) in the presence of water void of dissolved oxygen reacts to form magnitite (Fe_3O_4) plus hydrogen gas. Once dissolved oxygen is introduced, rust (Fe_2O_3) is formed ($4Fe_3O_4 + O_2 \longrightarrow 6Fe_2O_3$). Dissolved oxygen may be purged from water by heating it. In marine steam plants, this is accomplished in a de-aerating heater. However, small amounts of dissolved oxygen usually remain in the water after de-aeration. The remaining oxygen must be removed by adding chemicals called oxygen scavengers. A typical sequence of events involving oxygen scavengers is shown below:

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

$$4Fe_3O_4 + O_2 \longrightarrow 6Fe_2O_3$$

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$2N_2H_2 + O_2 \longrightarrow 2H_2O + 2N_2$$

$$2N_2H_2 + 6Fe_2O_3 \longrightarrow 4Fe_3O_4 + 2H_2O + 2N_2$$

In step one solid iron in the absence of oxygen is converted to a magnitite film (Fe_3O_4). The film forms over metal surfaces protecting those surfaces from further corrision. The introduction of oxygen in step two converts the protective film to rust (Fe_3O_3). The effect of adding an oxygen scavenger (Na_2SO_3) is shown in step three. Oxygen is removed when it reacts with sodium sulfate to form sodium sulfite (Na_2SO_4). Steps four and five show the result of adding an oxygen scavenger called hydrazine. Hydrazine (N_2H_2) not only scavenges oxygen as shown in step four, but also converts rust to the protective Fe_3O_4 as shown in step five. Compounds formed by reactions between oxygen and oxygen scavengers become non-adhering sludge

and are subsequently removed at blowdown. Another of the tests conducted on marine water determines the amount of oxygen scavenger present in the water. Like phosphates, scavengers remain in the water until consumed. The oxygen scavenger test identifies the time when additional scavenger must be added.

CONCLUSION

The health and longevity of marine water systems are maintained by periodic and conscientious water analysis programs. Good internal water treatment programs have five main objectives:

1. To prevent scale formation by properly treating incoming feed water.
2. To render suspended matter in system water nonadherent by converting it to sludge.
3. To eliminate dissolved oxygen from feed water.
4. To prevent boiler corrosion by maintaining proper pH values.
5. To permit reasonable concentrations of dissolved and suspended solids in the boiler water without causing carryover.

While our discussion suggests only salt water to exhibit adverse effects upon propulsion systems, fresh water also contains minerals. Although quantities of minerals or their variety may not be as great in fresh water, those that are found can also reign havoc. Ships operating on the Great Lakes should have ongoing water testing and treatment programs.

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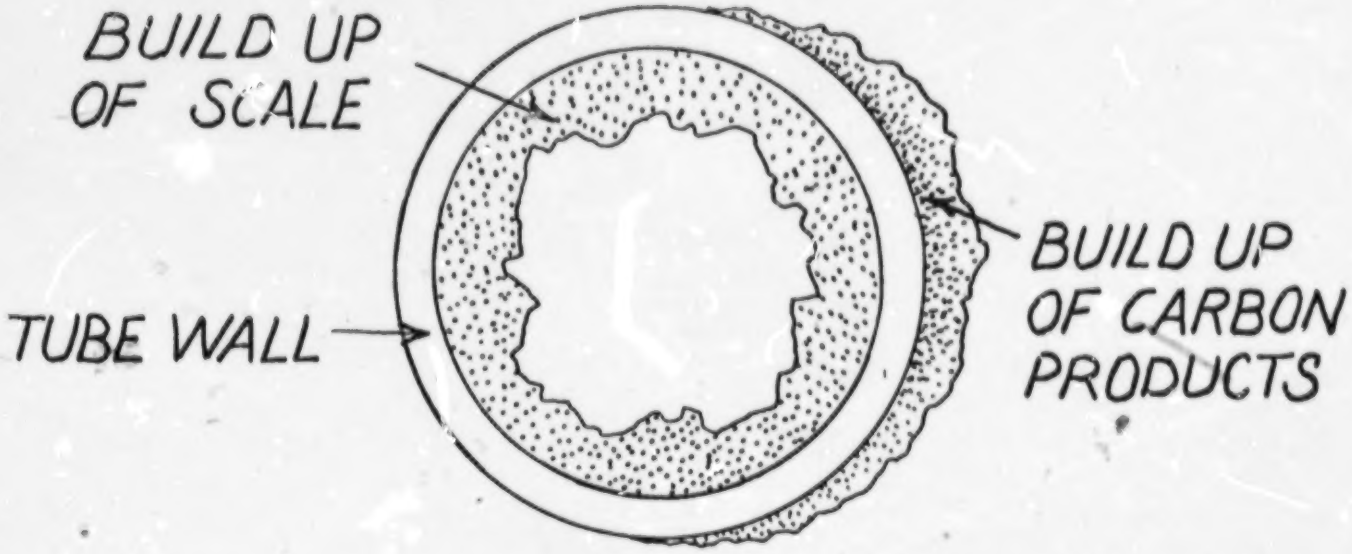

FIGURE 3. Coating on the fireside and waterside of a boiler

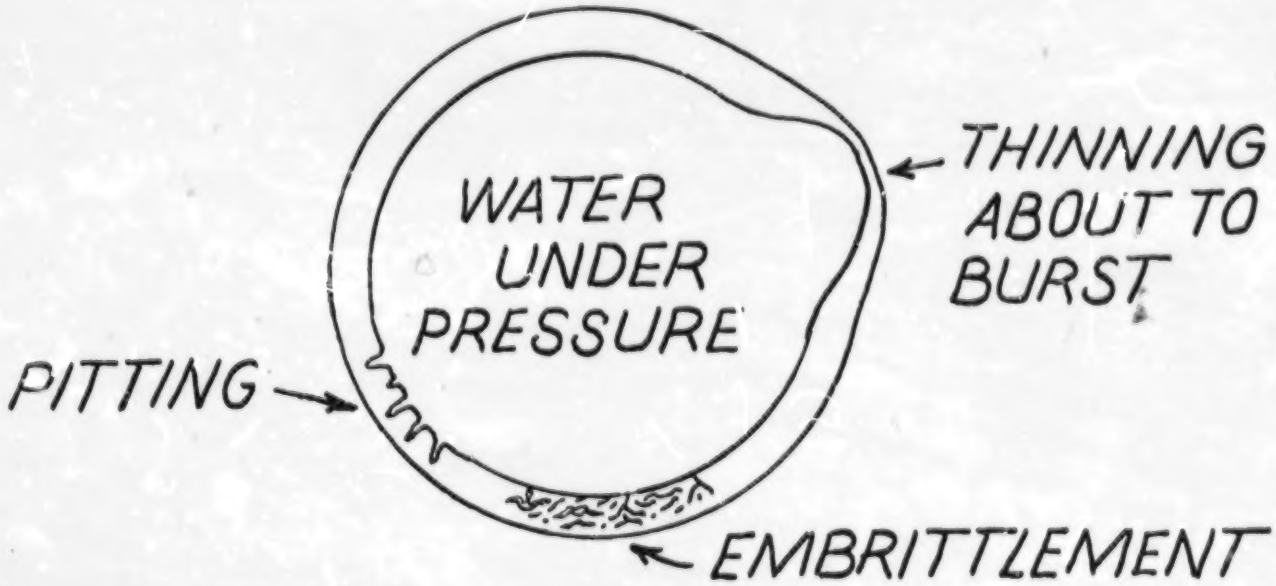

FIGURE 6. The results of corrosion (structural weakening due to physical and chemical causes)

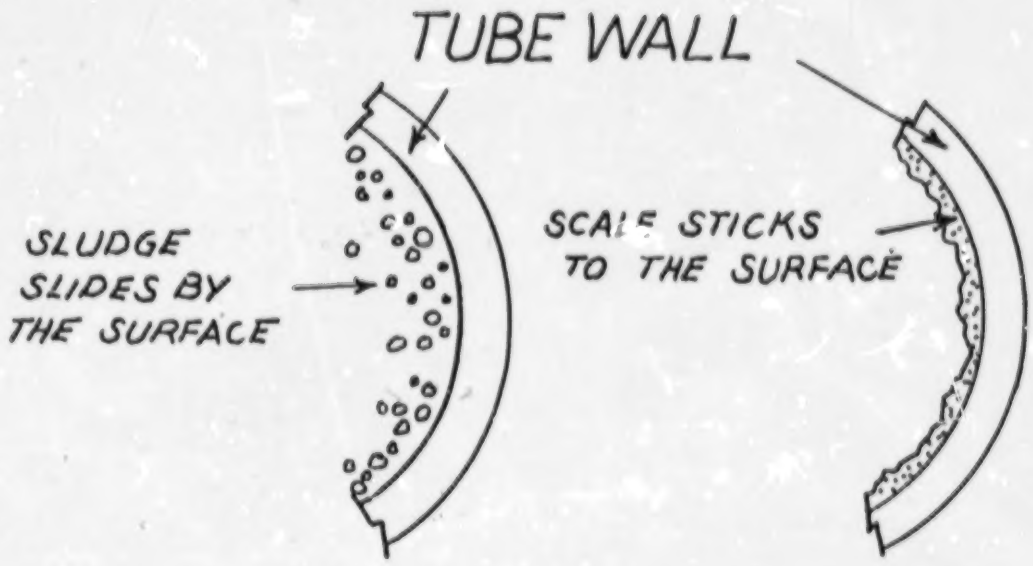

FIGURE 4. Scale and sludge effect on boiler tubes

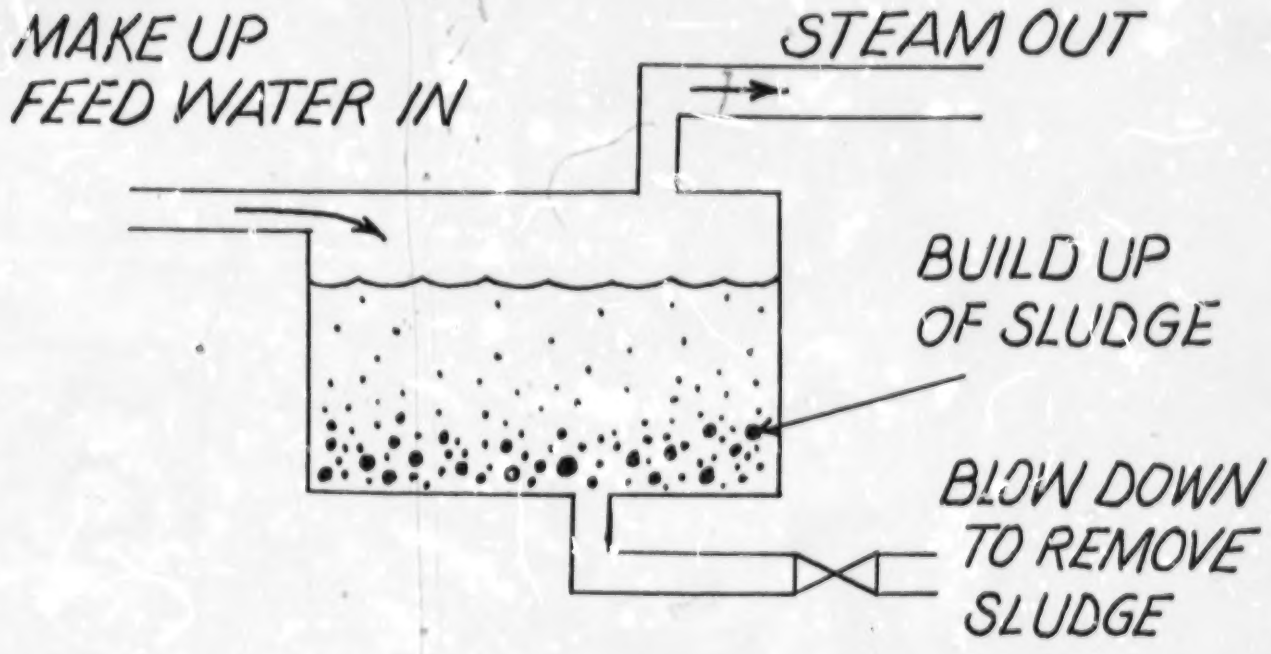

FIGURE 5. Sludge buildup in boiler water

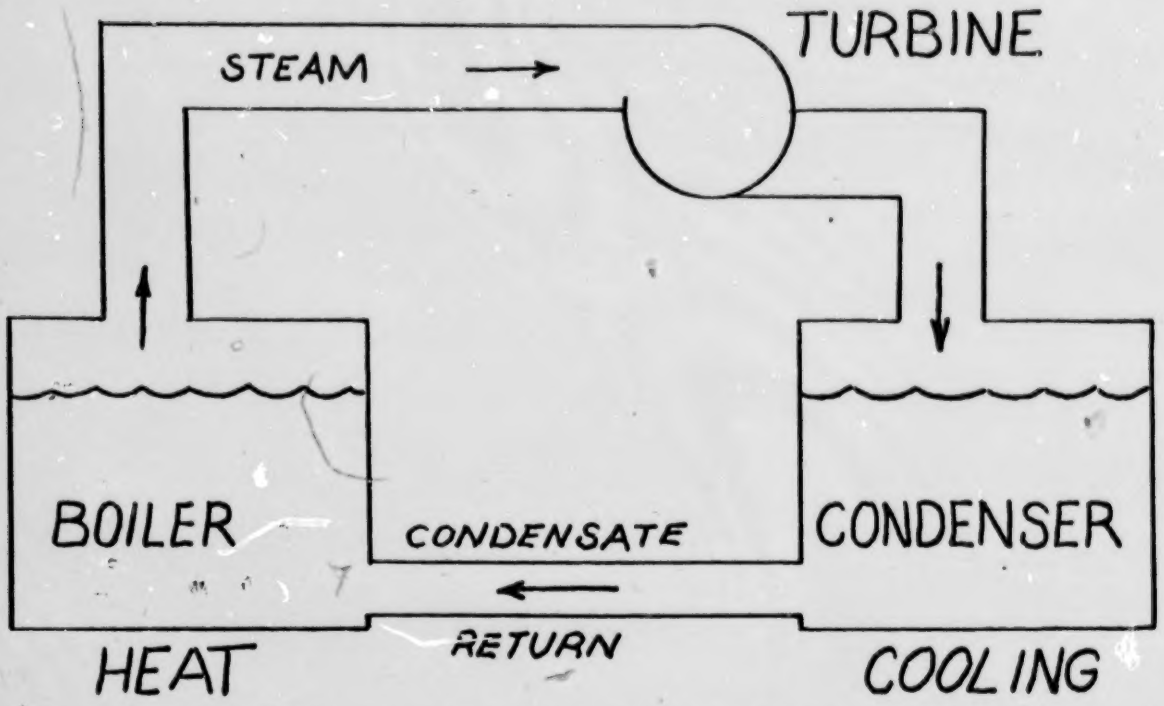

FIGURE 1. A schematicisized marine boiler system

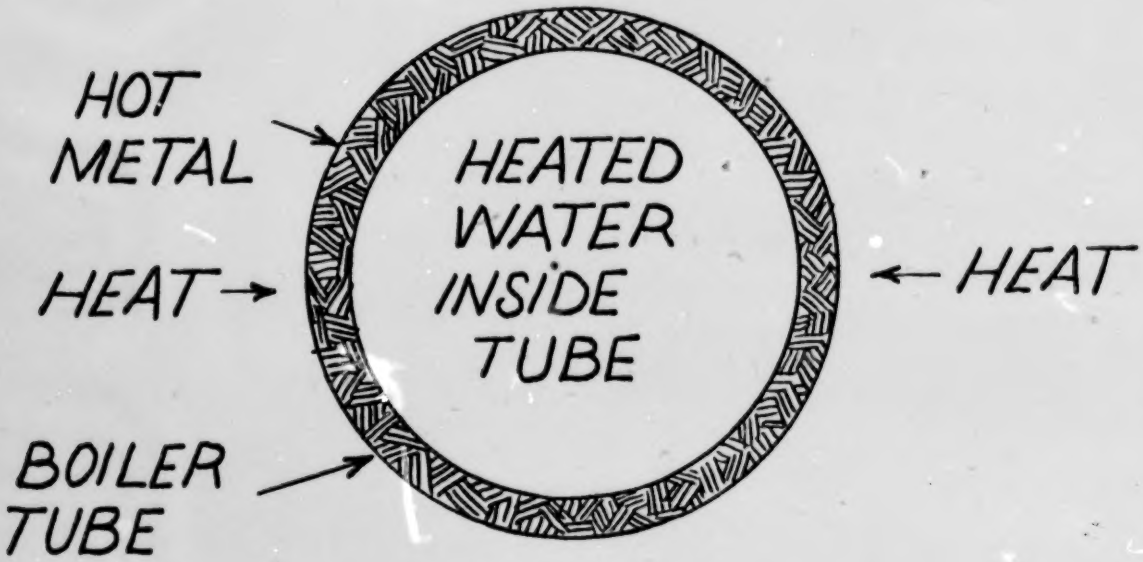

FIGURE 2. A boiler tube in cross section